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C-O bond hydrogenolysis vs C=C group hydrogenation of furfuryl alcohol: Towards a sustainable synthesis of 1,2-pentanediol

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The conversion of furfuryl alcohol into 1,2-pentanediol and tetrahydro furfuryl alcohol by aqueous phase hydrogenolysis using highly active supported ruthenium catalysts is a promising sustainable route for substituting the petro based production processes. An on-line analysis of the reaction, performed by ATR-IR spectroscopy, is necessary to show the formation of solid deposits during the reaction.

Nowadays, non-renewable fossil resources are the common basis for the production of chemicals and fuels. Crude oil is playing a key role in the production of hydrocarbons which are in turn the platform for the production of important base and fine chemicals. In this context, 1,2-pentanediol (1,2-PeD) is currently produced via a cost-intensive multistep route by selective oxidation of pentene to pentene oxide and a subsequent hydrolysis.[1, 2] The diol is frequently used as a monomer for polyesters, as a key intermediate of low-toxic microbicides[1] and as an ingredient of various cosmetic products[3].

Biomass will surely play an important role in modern chemical industry because approximately 170 quadrillion kilograms are produced by photosynthesis every year, but only a small percentage is used.[4, 5] In the next years, the rising demand for crude oil will lead to an increasing shortage so that the displacement of exhaustible raw materials through biomass is clearly desirable as a sustainable source for energy and organic carbon. Polysaccharides like cellulose or hemicellulose are the major part of biomass, consisting of C_5- or C_6-monosaccharides. While the direct selective conversion of cellulose into valuable chemicals is still a challenging research topic,[6, 7] various bulk chemicals like furfuryl alcohol (FA) are already produced from biomass via established production routes.[8] Furfuryl alcohol can be produced via hydrogenation of furfural or 5-hydroxymethylfurfural (5-HMF) and is able to be converted into various valuable alcohols.

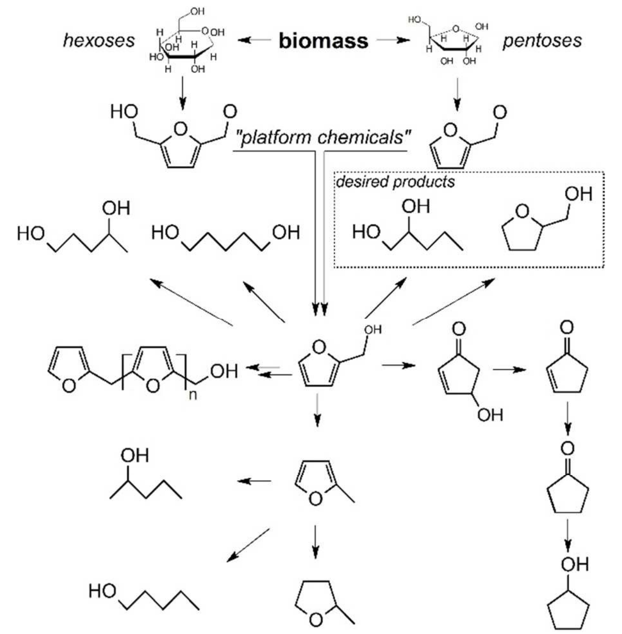

Figure 1 Simplified reaction network of the main components during aqueous phase hydrogenolysis of furfuryl alcohol.

Figure 1 presents a simplified reaction network including the main components in the aqueous phase hydrogenolysis of FA. One well-known route is the conversion into tetrahydro furfuryl alcohol (THFA) which can be done very selectively using ruthenium at low temperatures.[9] The subsequent conversion into 1,5-pentanediol is also receiving increasing interest.[10] In the past years, only small attention was paid to the conversion into 1,2-pentanediol. So far most of the catalysts reported for the hydrogenolysis of FA are lacking of disadvantages concerning their toxicity (e.g. copper chromite[11, 12]) or their need of additives or special solvents (e.g. Adams's catalyst[13]). This is clearly not desirable for a green and sustainable chemistry, summed up in the popular "12 principles of green chemistry"[14]. In contrast to aforementioned catalysts, supported ruthenium catalysts are non-toxic and are stable against water under hydrothermal conditions. Zhang et al. have recently reported formation of 1,2-PeD when using ruthenium supported on manganese oxide.[15] However, the industrial availability and applicability of these catalyst supports are limited. Hence, the usage of stable and available supports is obviously. This work is presenting the performance of ruthenium supported on alumina, silica as well as carbon (table 1). Additionally, because the formation of carbon in biomass based reactions is often overlooked we applied on-line ATR-IR spectroscopy during FA hydrogenolysis to get insight in the role of such species during the course of the reaction.

Table 1 Reaction time and selectivity of the main products at full conversion in aqueous furfuryl alcohol solutions using different catalysts.

catalyst	disp. / %	selectivity *1,2-PeD /%* *(TOF /s^{-1})*	 *THFA /%* *(TOF /s^{-1})*	 *others /%*	 *sum /%*	t */min*
5Ru/C[a]	35	20 (0.07)	49 (0.16)	11	80	45
10Ru/C[a]	17	21 (0.07)	60 (0.20)	16	97	45
10Ru/Al$_2$O$_3$[a]	22	26 (0.10)	53 (0.21)	11	90	30
10Ru/Al$_2$O$_3$[b,c]	22	32 (0.34)	57 (0.60)	11	100	60
10Ru/SiO$_2$[a,d]	-	14 (-)	32 (-)	27	73	200
Adams catalyst[13]	-	20 (-)	35 (-)	19	74	-

Reaction conditions:
T = 473 K, p_{H2} = 100 bar, agitation speed = 1000 rpm, m(cat) = 500 mg,
[a] c(FA) = 7.46 g/100ml, [b] c(FA) = 40 g/100ml, [c] m(Na_2CO_3) = 100 mg/100ml,
[d] m(Na_2CO_3) = 300 mg/100ml.

In this context, especially carbon and alumina supported catalysts are showing good selectivity values up to about 30% towards 1,2-pentanediol. Therefore they promise to be candidates with respect to the industrial implementation of this reaction. The other main product is tetrahydrofurfuryl alcohol (THFA) which is also of interest as a valuable product due to its use as a green solvent.[16] Beside 1,2-PeD two isomer diols, namely 1,4-pentanediol (1,4-PeD) and 1,5-pentanediol (1,5-PeD) are formedand it is interesting to see that especially the latter only in small amounts. In contrast to 1,5-PeD, which can be formed from THFA, experiments using THFA as a substrate indicate that the hydrogenolysis into the diols seems to be a parallel reaction of the hydrogenation to THFA under these conditions. This is also in agreement with the results of Zhang and coworkers,[15] who postulate two different active sites responsible for the hydrogenolysis towards 1,2-PeD and 1,5-PeD.

Apart from that, the reaction is often accompanied by formation of a yellow to red insoluble solid, responsible for the unbiased carbon balance in the liquid phase found by gas chromatography. By using attenuated total reflection infrared spectroscopy (ATR-IR) these solids can be identified as polymers of furfuryl alcohol exhibiting similar characteristic vibrational modes (figure 2). In addition to this, various dimers and oligomers are formed during the reaction. Since the self-polymerization of furfuryl alcohol is known to be catalysed by Lewis as well as Broensted acids[17] it is obvious that the formation of polymers is strongly enhanced by a low pH value of the reaction mixture as well as heterogeneous acid sites of the supporting material. In this context, NH3-TPD measurements of alumina and carbon supports show only weak acid sites indicated by an early desorption at about 423 K. The amount of ammonia adsorbed on carbon supports (5Ru/C: 0.35 mmol/g, 10Ru/C: 0.21 mmol/g) is higher compared to the alumina support (0.05 mmol/g), but the dependence on reaction parameters and catalytic activity seems to be way more pronounced than on acid sites of the support.

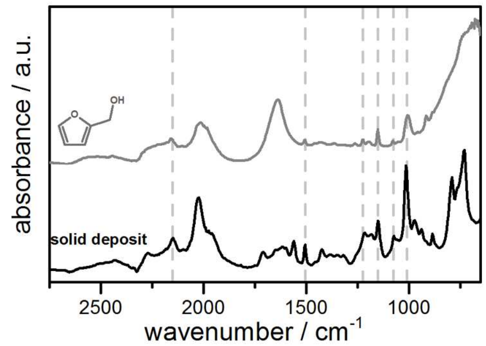

Figure 2 Infrared spectrum (ATR) of the insoluble solid deposit (below) in comparison to furfuryl alcohol (above, dissolved in water).

Although the polymerisation can be reduced by adding a homogenous basic additive (e.g. Na_2CO_3) the use of additives is not desirable and should be avoided if possible. Especially at lower hydrogen pressures desirable for the industrial realisation, the reaction parameters must be changed to milder conditions in order to avoid the formation of solid deposits. While FA concentration has a rather small influence on the 1,2-PeD selectivity, higher FA concentrations would favour the polymerisation, increasing the risk of forming solid deposits. So a rather small FA concentration of 5 wt.-% was chosen in the forthcoming experiments. In contrast to this, the reaction temperature is strongly influencing the selectivity of the desired diol 1,2-PeD as shown in table 2.

Table 2 Reaction time and selectivity of the main products at full conversion in aqueous furfuryl alcohol solutions at different reaction temperatures using 5Ru/C.

temperature / K	selectivity at full conversion *1,2-PeD /%* *(TOF /s^{-1})*	 *THFA /%* *(TOF /s^{-1})*	 *others /%*	 *sum /%*	t */min*
403	12 (0.08)	74 (0.49)	10	96	60
423	17 (0.15)	70 (0.62)	14	102	45
443	17 (0.15)	52 (0.46)	18	87	45
463	4 (0.04)	9 (0.08)	37	50	45

Reaction conditions:
p(H_2) = 30 bar, agitation speed = 1000 rpm, c(FA) = 5g/100ml,
m(cat) = 125 mg, PTFE reactor inlet. Selectivity sums greater than 100% are due to estimated calibration factors of side products.

Since the C-O bond hydrogenolysis is enhanced at higher reaction temperatures in comparison to the hydrogenation of the double bonds, lower temperatures favour the formation of THFA. While higher temperatures lead to a higher 1,2-PeD selectivity, they also promote side reactions, that do not depend on the catalyst and resultin a decrease of 1,2-PeD selectivity at higher temperatures. Beside the self-polymerization, the isomerization to 4-hydroxy-cyclopentanone (4-HCP) is the dominant reaction in this context. 4-HCP is the precursor compound for cyclopentanone which is hydrogenated to cyclopentanol.[18, 19] The hydrogenation of cyclopentanone to cyclopentanol is known to be inhibited by the furfuryl alcohol polymers so that the intermediate product reaches yields of about 15%.[20] These cyclopentanol rings are currently of increasing interest as another valuable product in this reaction chain. But regarding the use of high purity 1,2-PeD for cosmetics, the formation of side products is disadvantageous. An elaborate purification would be necessary, so intermediate reaction temperatures in the range of 130 to 150 °C are favourable due to a small formation of side product, although the selectivity might not be at its maximum.

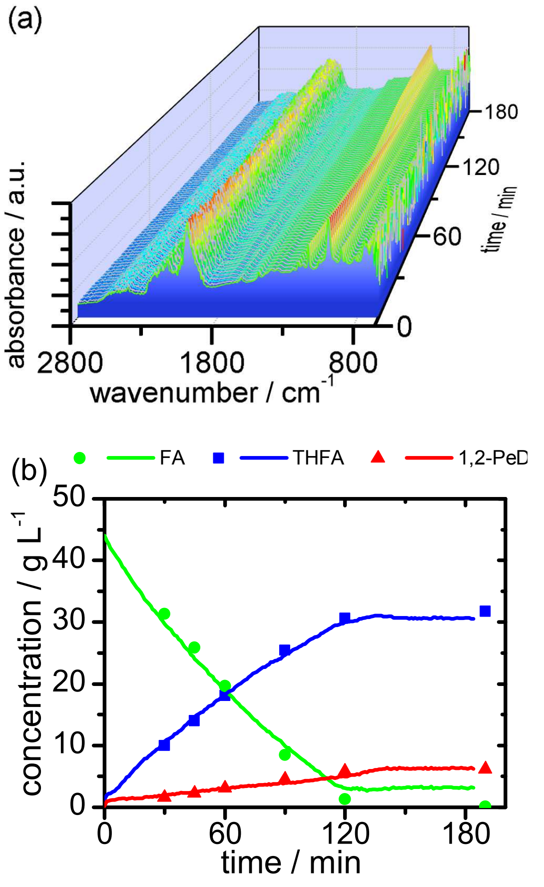

Figure 3 (a) Temporal change of ATR spectra (after subtracting the IR spectrum of the catalyst slurry) during the reaction. (b) Comparison of concentrations measured by ATR-IR (lines) and GC (symbols) during the reaction. Reaction conditions: 5%Ru/Al_2O_3, T = 403 K, c(FA) = 50 g/L, m(cat) =0.125 g, p(H_2) = 30 bar

In order to compete with the catalyst independent side reactions, high reaction rates are needed. Hydrogen consumption measured during the reaction is showing a nearly linear decay until full conversion during the reaction. This is presumably due to a strong adsorption of furfuryl alcohol over ruthenium, leading to a highly covered metal surface. In order to study these fast reactions a reliable and fast online process analysis method is required to monitor the reaction progress with a high temporal resolution. In this context, the aforementioned ATR-IR spectroscopy is a promising tool due to its fast measuring frequency without the need for taking and analysing offline samples. Although the strong IR absorption of water is challenging in aqueous systems, the experiments show that ATR-IR spectroscopy is able to detect and also quantify the main components of the reaction mixture when compared to the gc samples in a reliable way(figure 3).

The ATR spectroscopy confirms that almost constant decay of FA shortly before full conversion is reached. Nearby the full conversion of furfuryl alcohol the reaction rate decreases significantly.

A full conversion of FA is desirable due to formation of FA-water azeotropes, so that the subsequent separation of the product mixture is more complicated in presence of FA.[21] It is remarkable that that beside the detection of soluble hydrocarbons, the ATR probe head is also very sensitive on depositions of the insoluble solid polymers formed by the self-polymerization as shown in figure 2. This means, the ATR spectrometer can instantly detect formation of polymers at an early stage during the process. This is important to ensure a failure-free and safe process with regard to an industrial implementation of this biomass-derived reaction.

Conclusions

The aqueous phase hydrogenolysis of furfuryl alcohol represents a promising sustainable alternative for the production of 1,2-pentanediol. The hydrogenolysis can be successfully carried out by using highly active ruthenium catalysts supported on common materials like alumina or carbon. ATR spectroscopy is able to show the formation of poly(furfuryl alcohol) deposits during the reaction. Although the undesired polymerisation can be reduced by base additives this can also be done by adjusting the reaction conditions. Additionally to the detection of solid deposits ATR-IR spectroscopy is useful as an in-time process monitoring tool, helpful to improve the efficiency and safety of furfuryl alcohol hydrogenolysis.

Materials and Methods

Catalysis experiments are carried out using a 300 mL stainless steel batch reactor (Parr Instruments). The reactor is equipped with an external storage for a subsequent introduction of furfuryl alcohol (98%, Sigma Aldrich) into the catalyst-solvent slurry after being heated up. Catalysts are prepared by incipient wetness impregnation with a ruthenium precursor or supplied by Evonik Industries or Alfa Aesar. Dispersity is determined by CO pulse-chemisorption at 273K (TPD/R/O 1100, Thermo Finningan). Acid sites are characterized by temperature-programmed desorption of ammonia. During the reaction, liquid phase samples are taken and analysed by gas chromatography (GC as well as GC/MS). Additionally, the reactor can be equipped with a high pressure attenuated total reflection infrared spectrometer (Mettler Toledo ic45m, DiComp) for in situ infrared spectroscopy. Quantitative analysis of the infrared spectra is done by using the quantification module *icQuant* in the software package *icIR* (Mettler Toledo, version 4.0.641.1). The multivariant quantification model was trained using calibration samples at room temperature and also using spectra recorded under reaction conditions during offline samples.

Notes and references

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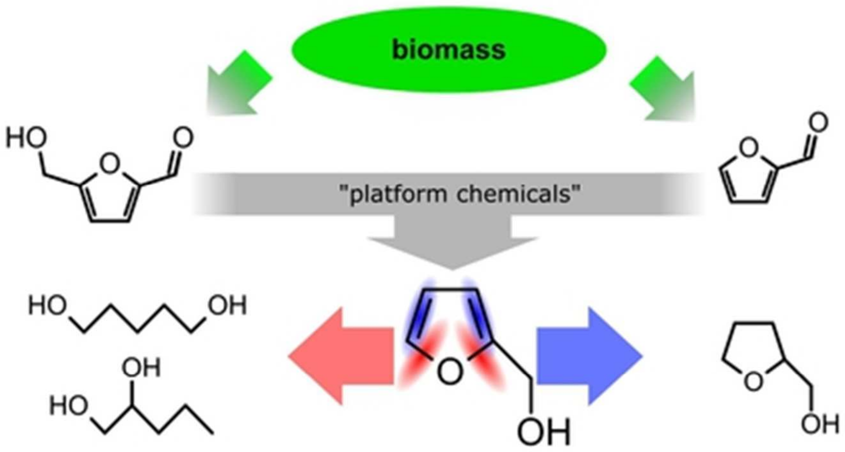

Using highly active supported ruthenium catalysts, the aqueous phase hydrogenolysis of furfuryl alcohol into 1,2-pentanediol and tetrahydro furfuryl alcohol is representing a promising sustainable route for substituting the petro based production processes.
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